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The investigation described in this thesis has included a study of the kinetics of the exchange of chlorine between chloride and tetrachloroplatinate (II) in aqueous solution. As the case in any exchange study it has been necessary to develop a radioactive tracer technique and separation procedure so that the extent of the exchange could be ascertained. By the determination of the extent of exchange as a function of time, the dependence of the rate of exchange upon a number of concentration variables was demonstrated. It was to be expected that the experimental exchange rate law would elucidate features of the mechanism of the process and the species which were involved.

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KINETICS OF CHLORIDE EXCHANGE IN AQUEOUS CHLORIDE-TETRACHLOROPLATINATE(II) SYSTEM

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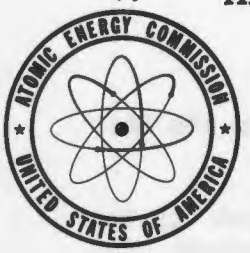

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KINETICS OF CHLORIDE EXCHANGE IN AQUEOUS CHLORIDE-TETRACHLOROPLATINATE(II) SYSTEM*

by

LeRoy F. Grantham and Don S. Martin

ABSTRACT

The exchange of chlorine-36 in systems containing Cl^-, $PtCl_4^=$, and $PtCl_3(H_2O)^-$ has been followed. Information about the reversible aquation of tetrachloroplatinate(II) is now available; i.e., the rate constants and equilibrium constant for the reversible reaction:

$$PtCl_4^= + H_2O \rightleftharpoons [PtCl_3(H_2O)]^- + Cl^-$$

When $[Pt(NH_3)_4](NO_3)_2$ was added, both platinum-containing anions were precipitated as a mixture of the compounds, $[Pt(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][PtCl_3(H_2O)]_2$. With chlorine activity added as chloride the extent of the exchange could be calculated from the specific activity of the precipitated mixture. Exchange experiments were carried out in the dark with freshly prepared potassium chloroplatinite (K_2PtCl_4) solutions and with aged solutions which had attained equilibrium with respect to the aquation represented in the above reaction. The extent of exchange provided by the above aquation mechanism was calculated from the rate expressions of the reactions. In systems with low $[PtCl_3(H_2O)]^-$ concentrations the calculated results were in agreement with experiment, precluding any second order exchange involving $[PtCl_4]^=$. An additional exchange was found which was first order in the $[PtCl_3(H_2O)]^-$ concentration, and independent of chloride concentration.

*This report is based on a masters thesis by LeRoy F. Grantham submitted June, 1954 at Iowa State College, Ames, Iowa. This work was performed under contract with the Atomic Energy Commission.

INTRODUCTION

The investigation described in this thesis has included a study of the kinetics of the exchange of chlorine between chloride and tetrachloroplatinate (II) in aqueous solution. As the case in any exchange study it has been necessary to develop a radioactive tracer technique and separation procedure so that the extent of the exchange could be ascertained. By the determination of the extent of exchange as a function of time, the dependence of the rate of exchange upon a number of concentration variables was demonstrated. It was to be expected that the experimental exchange rate law would elucidate features of the mechanism of the process and the species which were involved.

The discovery and preparation of radioactive nuclides have provided a valuable tool for investigations of the mechanisms of chemical reactions. A unique advantage of the radioactivity lay in the possibility of tagging a certain fraction of atoms in a complex chemical system. The fate of the tagged fractions could be followed throughout the course of a chemical experiment. If radioactivity was found in some chemical form, it was known that atoms from the originally tagged fraction had been transformed into this form. Such transformation could, therefore, even be demonstrated in situations in which no chemical change could be observed, i.e., in systems at chemical equilibrium. In these cases the rates of the inverse processes involved in chemical equilibrium could be evaluated.

An isotopic exchange reaction concerns the interchange of the atoms of an element between two or more chemical forms which may or may not be at equilibrium with respect to one another. If the chemical system is not in an equilibrium condition, then the course of the reaction may be followed by several methods, e.g., the chemical analysis for a component, the measurement of some appropriate physical property, such as conductivity or absorptivity, or the determination of concentration of a radioactive tracer in one of the components. In a system, undergoing no observable change, the isotopic tracer offers the **only** means for evaluating the rates of chemical processes which may be occurring.

A comprehensive bibliography of exchange work available before the end of 1949 is included in the appendix of "Radioactivity Applied to Chemistry" (1) by Wahl and Bonner. Another excellent book in the field is "Introduction to Radiochemistry" (2) by Friedlander and Kennedy.

One of the earliest of exchange experiments was carried out by Hevesy and Zechmeister (3) in 1920 with lead exchange between two salts. The radioactive nuclide of Pb^{212}(ThB) was used to tag $Pb(NO_3)_2$ which was dissolved in an aqueous solution containing $PbCl_2$. The appearance of radioactive lead in $PbCl_2$, crystallized immediately from solution, indicated a rapid exchange. Hevesy and Zechmeister (4) used the same nuclide to prove

that there is a rapid exchange of lead between $Pb(C_2H_3O_2)_2$ and $Pb(C_2H_3O_2)_4$ in acetic acid solution. Some of the earliest halogen exchange experiments (5, 6, 7, 8, 9) proved that almost instantaneous isotopic equilibrium was attained between halogens and their halides in aqueous solution. The following mechanism was proposed for the reaction:

$$X_2 + X^{-*} \rightleftharpoons X_3^{-*} \rightleftharpoons X_2^* + X^-$$

Also, several compounds (10, 11), i.e., SbI_3, $AsBr_3$, $SnBr_4$, exchanged halide quite rapidly with halogen in nonaqueous media, e.g., CCl_4. For this sort of exchange, the mechanism below was proposed:

$$MX_3 + X_2^* \rightleftharpoons MX_5^* \rightleftharpoons MX_3^* + X_2$$

Still other workers (12, 13, 14, 15) have found that the halogen in the $[ClO_2]^-$, $[ClO_3]^-$, $[ClO_4]^-$, $[BrO_3]^-$, $[IO_3]^-$, and $[IO_4]^-$ does not exchange rapidly with the corresponding tagged halide ion in either acidic or basic aqueous solution.

It has been well established that platinum, in either of its relatively stable oxidation states of +2 and +4, forms many coordination compounds. Platinum(II) usually has the coordination number 4 and a square, coplanar arrangement of bonds; whereas, platinum(IV) invariably has the familiar octahedral arrangement of ligands. The complexes of both oxidation states are of the inert type as defined by Taube (16), and replacement reactions are normally very slow. Actually, several hundred of these coordination compounds had been prepared and characterized before 1893. Werner (17) included the isomers of these complexes of platinum, together with those of cobalt and other elements, in his classical proposals on geometrical arrangements. The transfer of these ideas to an electronic basis was largely due to Sidgwich (18) and Lowry (19) and later clarified by Pauling's (20) description of hybrid orbitals of the transition elements.

A series of typical platinum(II) coordination complexes can be prepared with chloride and ammine ligands. All possible members of the series with the general formula $[Pt(NH_3)_{4-n}Cl_n]^{n-2}$ $(0 \leq n \leq 4)$ can be prepared. In the case of $Pt(NH_3)_2Cl_2$ both the cis- and trans- stereoisomers have been prepared and identified unambiguously by x-ray crystallography. The last member of the series, $[PtCl_4]^=$, was chosen for this particular investigation. Potassium tetrachloroplatinate(II) forms red, tetragonal crystals that are moderately soluble in water. A freshly prepared aqueous solution of K_2PtCl_4 is a deep red but turns brown upon standing.

The exchange of pltainum between cis-tetrachlorodiammineplatinum(IV) and hexachloroplatinate(IV) was studied by Grunberg and Filinow (21, 22). In this case, very dilute hot solutions were used; the reaction was stopped

by cooling the solution in an ice bath and filtering off the crystallized cis-tetrachlorodiammineplatinum(IV). Platinum-199, with a half-life of 31 minutes, was introduced into the hexachloroplatinate(IV) before the two platinum complexes were dissolved together in an aqueous solution. The results showed that no exchange could be detected; the half-time of exchange was reported to be long compared to the half-life of the nuclide.

Christian (23) proved that the exchange of platinum did not occur when tetrachloroplatinate(II) and hexachloroplatinate(IV) were dissolved together in solution.

Several exchange reactions involving the ions (or radicals) complexed to platinum have been investigated by Grunberg and Nikol'shaga (24) in connection with complex stability studies. This work has been seen only in abstract form. The CN^-, Cl^-, Br^-, and I^- ligands in complexes of +2 platinum were allowed to exchange with the ions according to the following reaction:

$$[PtX_4]^= + X^{-*} \rightleftharpoons [PtX^*X_3]^= + X^-$$

The radioactive nuclides Cl^{38}, Br^{80} plus Br^{82}, I^{128} and N^{13} in CN^- were used for tagging. The concentration of reactants was such that the tracer atoms were distributed equally among the two substances at equilibrium. As a separating agent these workers used tetraammineplatinum(II) chloride when working with the halide exchange but resorted to benzidine hydrochloride to stop the cyanide exchange. The results were presented as the times required to attain an equilibrium distribution of the activity. They reported 5 minutes for CN^-, 25 minutes for I^-, 40 minutes for Br^-, and an indefinite length of time for chloride. They found the chloride exchange was only 11% complete after 60 minutes of elapsed time. Using Cl^{38} (half-life 38 minutes), they found that virtually all of the activity had decayed before the exchange was complete. In conclusion of his experiments Grunberg attempted the reverse exchange for CN^- and $[Pt(CN)_4]^=$ complex. When untagged potassium cyanide was placed in the presence of a solution of $K_2Pt(CN)_4$; it was found that a very rapid, 1st order, equilibrium was reached. Grunberg, however, did not take into consideration the possibility of a photochemical effect. Other workers (25, 26) have found that some related exchange reactions are very photosensitive.

Another case, in which the exchange of ligands in a square, coplanar complex was measured, has been reported recently. Taube and Rich (27) found that $[AuCl_4]^-$ exchanged very rapidly with chloride ions in solution. The kinetics indicated three different paths for the process. The observed half-times proved to be a matter of 3 or 4 minutes depending on several conditions. The reaction appeared to have a definite pH dependence.

The present studies were undertaken following experiments performed by Christian (23). In her work she attempted to prepare high specific activities of platinum by means of a Szilard-Chalmers (28) reaction. For example $Pt(NH_3)_4Cl_2$ was irradiated by the 70 Mev bremsstrahlung of the Iowa State College synchrotron to give Pt^{196} (γ,n) Pt^{195}. A separation of the platinum activity from the dissolved samples was attempted by the addition and separation of $PtCl_4$ = carrier. At no time was the activity completely removed; repeated separations continued to bring down significant quantities of activity. Apparently, a portion of the radioactive platinum was introduced into complexes which exchanged only slowly with the carrier and was not completely separated with it. The nature of the species in the solution was not known and a search of the literature revealed that they had not been satisfactorily characterized. The present work is an attempt to get basic information on a simple system.

There has been evidence in the literature that the aquation of $[PtCl_4]^=$ can occur. For example, an amorphous substance with a composition corresponding to the formula $HPtCl_3 \cdot H_2O$ was prepared by Nilson (29) by evaporation of a solution of $H_2PtCl_4 \cdot x\,H_2O$ over sulfuric acid and potash. Miolati and Pendini (30) reported the preparation of Ag_2PtCl_3OH. Friend (31) referred to the two acids, H_2PtCl_3OH and $H_2PtCl_2(OH)_2$.

Recently, in his work with solutions of platinum(II) Flikkema (32) obtained quantitative evidence that aquation complexes were formed when tetrachloroplatinate(II) was allowed to remain in aqueous solution at room temperature.

$$[PtCl_4]^= + H_2O \rightleftharpoons Cl^- + [PtCl_3(H_2O)]^- \rightleftharpoons [PtCl_3OH]^= + H^+$$

$$[PtCl_3(H_2O)]^- + H_2O \rightleftharpoons Cl^- + PtCl_2 \cdot 2H_2O \rightleftharpoons [PtCl_2OH(H_2O)]^- + H^+$$

The existence of these compounds was demonstrated by a pH titration of the solutions. $PtCl_2 \cdot 2H_2O$ was a somewhat stronger acid than $[PtCl_3(H_2O)]^-$. The second aquation reaction appeared to be base catalysed; however, over a period of a few days it was insignificant as long as the solution remained acidic.

MATERIALS

Platinum was obtained as the foil from J. Bishop & Co. and reagent grade tetrachloroplatinic(IV) acid from Mallinchrodt Chemical Company. Platinum compounds were prepared as indicated below. All other chemicals were of reagent grade quality.

Platinum Black Due to the cost of platinum a satisfactory method had to be found to recover the element from all solutions. This was accomplished by precipitating platinum black from a neutral or slightly alkaline solution with magnesium powder. To remove any excess magnesium, the final solution was made quite acid in HCl. It was found that by boiling the strongly acid solution the finely divided colloidal platinum black coagulated to form an ideal precipitate for filtering or decanting. If desired, this washed platinum black could be boiled with nitric acid to remove other impurities. No attempt was made to separate any noble metals since chemically pure platinum was used in the beginning and no noble metals (except silver) were introduced throughout the entire exchange procedure. To remove any silver chloride that might be present, the platinum black was dissolved in aqua regia, the solution was diluted and the residual silver chloride precipitate was filtered out. This procedure left the recovered platinum in a very pure, ready accessible form.

K_2PtCl_4 Potassium tetrachloroplatinate (II) was prepared by reducing potassium tetrachloroplatinate(IV) which in turn was prepared from platinum black by a procedure recommended by Mellor (33).

Several methods of reducing platinum from a valence of four to two are known. Sulfur dioxide (34), potassium oxalate (35), potassium hydrogen sulfite (36), hydrogen sulfite (37), copper (I) chloride (38), and tin(II) chloride (39), are reagents commonly used with the tetravalent platinum. Even the thermal decomposition of tetrachloroplatinic(IV) acid has been used (40).

The relative purity of the final product is dependent upon the reagent used in the reduction. As indicated in "Inorganic Preparations" (41) a sulfur dioxide reduction will give a product pure enough for most uses; but, the danger of sulfite-complex contamination of the final product exists. It is very difficult to determine the exact end-point of the reduction. If not enough SO_2 is added some K_2PtCl_6 will remain; on the other hand if too much SO_2 is added unwanted reduction products and sulfur complexes occur.

Tin(II) chloride is a very effective reducing agent but unfortunately some type of a tin complex may be formed with tetrachloroplatinate(II). Haldar (42) suggested that this complex explains the peculiar incident in

which the platinum(II) will extract into butylacetate (made strongly acid with HCl) only when tin is present in solution. Work in this laboratory in conjunction with this problem proved that even freshly prepared tetrachloroplatinate(II) (prepared by sulfur dioxide reduction) would not extract until stannous chloride was added to the solution.

The oxalate procedure suggested by Vezes proved to be the most satisfactory reducing agent. It is possible to weight out both $K_2C_2O_4$ and K_2PtCl_4, the two reactants, thus, several possible contaminating materials formed from excess reagents could be eliminated. Excess potassium oxalate will yield a grayish green, insoluble, unstable $K_2Pt(C_2O_4)_2$ which reduces to platinum black upon prolonged heating.

$$K_2PtCl_4 + K_2C_2O_4 \longrightarrow K_2PtCl_4 + 2CO_2 + 2KCl$$

The only contaminating by-product of the reaction is the potassium chloride formed. This can be removed by recrystallizing the potassium tetrachloroplatinate(II) from water.

In the absence of a catalyst the reduction of $[PtCl_6]^=$ to $[PtCl_4]^=$ by $[C_2O_4]^=$ was very slow. It was found, however, that platinum black catalysed the reduction and gave a complete reaction in 30 minutes whereas, previously, several hours were required to reduce a few grams of hexachloroplatinate(IV). It was found helpful to allow the reactants to reflux so that a minimum volume of water was used.

Analysis of the final salt, recrystallized from an alcohol acetone mixture, indicated that the oxalate method of reduction was not only efficient but effective in yielding a very pure product. Platinum was deposited from a 2% sulfuric acid solution onto a platinum cathode with a Sargent-Slomin electro-analyser. The standard Mohr titration was used to determine the amount of chloride present. The results of the analysis are given in the table below:

Table I. Analysis of potassium tetrachloroplatinate(II).

Element	Wt. of Sample	Per cent Found	Calculated Per cent
Pt	335.3	46.73	
Pt	444.2	48.47	47.13
Pt	435.3	46.73	
Cl	444.2	32.32	34.15
Cl	398.3	34.49	

It should be mentioned at this time that potassium tetrachloroplatinate (II) is unstable in a water solution; therefore, this shorter reduction time proved very helpful in obtaining a product which contained very small amounts of hydrolysis product contaminants. This will be discussed later in more detail.

$Pt(NH_3)_4(NO_3)_2$ The repeated addition of ammonia (43) to a solution of tetrachloroplatinate(II) yielded tetraamineplatinum(II) chloride as a major product. Recrystallization from ice water gave long needle-like crystals that were slightly yellow in color. When a solution of this salt was poured into an ether, alcohol, and acetone mixture, a white, voluminous precipitate separated. Analysis of this precipitate indicated that a very pure product was obtained.

So that the chloride activity would not be diluted in the exchange the $Pt(NH_3)_4Cl_2$ was converted to another salt. Preparation of the perchlorate was attempted but proved quite unsatisfactory. Instead of preparing the nitrate as suggested in Mellor (44) it was decided to use an exchange resin in the nitrate cycle to replace the chloride ions in the original salt. Very satisfactory results were obtained with Dowex I anion resin.

Radioactive Chlorine-36 The chlorine-36 was obtained from the Isotopes Division, United States Atomic Energy Commission, Oak Ridge, Tennessee. The specific activity of the isotope was 0.23 millicurie per gram. It was shipped as 1.46 N Hydrochloric acid. The radiochemical purity was greater than 99%. This particular isotope was very suitable as a tracer since its half-life was 4.4×10^5 years. Thus all errors due to decay were eliminated. The radioactivity consisted solely of a beta-particle with a maximum energy of 0.72 Mev. Reagent grade potassium chloride was used as a carrier to reduce the specific activity of the original material.

EQUIPMENT

Beta-Ray Counters A TCG-1 end-window Geiger-Muller counter tube, manufactured by Tracerlab Inc., was used to measure the activity in the samples. The thickness of the mica window was 2.3 mg/cm^2. This tube was mounted in a lead housing to minimize the background counting rate. The sample rack in the lead housing was adjusted so that the first shelf was approximately 7 mm. from the tube window. A Berkeley model 100 decimal scaler in conjunction with a semi-automatic electrical timing device was used to record the pulses. The counting arrangement was estimated to be about 10% efficient.

Filtering Apparatus Conventional filtering techniques were not convenient for the preparation of radioactive counting samples. Often these techniques were slow and would not give an evenly deposited precipitate that could be conveniently weighed and mounted. Therefore, a special filtering apparatus

was used. By using this method, one could prepare samples that were readily washed and dried to yield a very uniform counting sample.

The apparatus was constructed in the following manner. One end of a glass sealing tube, 3.3 cm. inside diameter, was cut off flush with the fritted glass disc and polished even with it. To the other end of the tube, which formed the bowl of the filter funnel, 5 cm. of 0.6 cm. glass tubing was sealed.. Filtration could then be effected by means of suction from an aspirator. Filter discs approximately 3 cm. in diameter were cut from Whatman #50 filter paper. One of these filter papers was placed on the fritted glass disc and a 2.5 cm. (inside diameter) glass chimney was held securely in place above it by means of rubber bands. After filtering, the samples were washed with alcohol and ether prior to drying.

Reaction Vessels Preliminary experiments had proved that the exchange reaction was photosensitive; therefore some method had to be found to exclude light from the solution while the exchange was in progress. It was more convenient to allow several individual samples to age separately than to obtain the samples by extracting portions of the entire solution at various times in the dark. Small 17 x 55 mm. dilution tubes and 18 x 150 mm. culture tubes were covered with black opaque Scotch Electrical tape and fitted with two hole rubber stoppers. After the solutions were placed in these reaction vessels, the tube was completely sealed with tape; thus, allowing the solutions to age in total darkness.

Constant Temperature Bath A constant temperature bath was employed. The bath temperature was controlled to $25.00 \pm 0.05^{\circ}$. A Sargent mecurial thermoregulator in conjunction with a Precision Scientific Co. control box made up the necessary electrical regulating devices.

pH Meter A Beckman model "G" pH meter was used in all of the pH titrations. Neither of the electrode leads were shielded; therefore, all readings were made with the door closed. Ordinarily the pH range varied from four to ten; consequently, a buffer solution of pH 7 was used to zero the instrument. No corrections were applied to the values at high pH even though an ordinary glass electrode was used.

Exchange Resin Dowex I anion exchange resin was charged with nitrate by using nitric acid and sodium nitrate. The resin particles varied in size from 20-40 mesh. Constant checks were made throughout the preparation of the tetraammineplatinum(II) nitrate to insure that no chloride was present after the solution had passed through the resin.

EXPERIMENTAL PROCEDURE

Preparation of Solutions The preparation of the reagent solutions was not identical in all cases. For example, with a freshly prepared solution of

tetrachloroplatinate(II), the radioactive HCl tracer was added to a standard KCl solution of known concentration. After the solution was thoroughly mixed, it was pipetted into the reaction vessels. A weighed amount of K_2PtCl_4 was dissolved in a small amount of H_2O. As soon as the crystals had dissolved, the solution was diluted in a volumetric flask and shaken to insure mixing. Aliquots of these solutions were then pipetted into the reaction tubes. The time at which the two solutions were mixed was considered as the zero time for exchange.

When working with an aged solution of tetrachoroplatinate(II), the desired amount of potassium chloride was dissolved with the potassium tetrachloroplatinate(II). This solution was allowed to age at 25° C for several hours. The radioactive tracer was then added to the solution and mixed thoroughly with it. The solution was pipetted into reaction vessels where the exchange was allowed to proceed. Zero time for the exchange was the time at which the radioactive tracer was added. The amount of chloride in the tracer was negligible compared to the amount already present in the solution as carrier. At the minimum chloride concentration, the maximum amount of chloride in the tracer solution added was less than 2% of the total chloride concentration. The total volume change in the solution due to the addition of the radioactive tracer was also negligible; maximum volume added was less than .01% of the total volume. Under these conditions the solution was at chemical equilibrium throughout the exchange.

Quenching the Reaction When the appropriate time for exchange had elapsed, a reaction vessel was untaped and tetraammineplatinum(II) nitrate was added to precipitate $Pt(NH_3)_4PtCl_4$, Magnus' salt (45). The green precipitate started to come down within 30 seconds. It was found however that by allowing 5 minutes for precipitation, approximately 70% of the salt would be retained on the filter paper. After 24 hours the precipitate weight corresponded to 95% recovery. In preparing the samples 5 minutes for precipitation were allowed.

Magnus' salt is listed as being only slightly soluble in water. A weighed amount of the salt was placed in a 500 ml volumetric flask and enough water was added to make 500 ml of solution at 25°C. The solution was stirred constantly at this temperature for 4 hours. The precipitate was filtered and weighed. The solubility of Magnus' salt was found to be 0.029 grams per liter. In another case the precipitate was separated after two days contact with the solution, nearly identical results were obtained.

Since the recovered weights of precipitates varied considerably, it was necessary to determine the effect of self-absorption and scattering of the radiation on the final counting rate. This was accomplished by precipitating various weights of tagged tetrachloroplatinate(II) as tetraammineplatinum(II) tetrachloroplatinate(II). In Figure I the observed specific

activity (counts/min mgCl) has been plotted against thickness expressed as mg of precipitate per square cm. The results show that by preparing samples of approximately 6 mg/cm^2 (which corresponds to a total weight of approximately 50 mg) a maximum specific activity was observed.

Filtering and Washing The Magnus' salt was filtered using the apparatus previously described. The precipitate was washed three times with water, three times with alcohol and three times with ether. By the use of a forceful jet of water during washing, it was possible to stir up the precipitate from the filter paper and allow it to resettle. This procedure facilitated washing and yielded a sample of uniform thickness. The filter disc had been washed, dried, and weighed in identical manner previously.

Drying and Weighing The samples were dried in a 70° oven for at least one hour and another hour was allowed for them to cool and come to constant weight. They were weighed on an Ainsworth & Sons Chain-Weight balance to the nearest tenth of a milligram.

It was found that the weight of the filter paper varied with the humidity of the air in which it was dried. Tare filter discs (filter discs on which samples were not precipitated) were carried along with the samples and reweighed to obtain the correction needed for determining the actual weight of precipitate. Table II indicates the accuracy of weighing as well as typical correction data. Sequence weighings were made a day apart. Notice the extreme weight change in the 4th weighing which was brought about by high atmospheric humidity. The table indicates that the maximum weighing error is approximately 0.1 mg.

Table II. Filter disc correction factors

	Weight of disc on various weighings				Change in weight		
Sample#	1st.	2nd.	3rd.	4th.	2nd.	3rd.	4th.
1.	70.37	70.33	70.34	70.95	-.04	-.03	.58
2.	68.90	68.85	68.75	69.56	-.05	-.15	.66
3.	66.30	66.30	66.25	67.08	-.00	-.05	.78
4.	69.68	69.66	69.65	70.41	-.02	-.03	.73
5.	66.70	66.67	66.64	67.51	-.03	-.06	.81
6.	68.59	68.54	68.53	69.26	-.05	-.06	.67
7.	68.71	68.63	68.65	69.43	-.08	-.06	.72
8.	70.59	70.53	70.57	71.18	-.06	-.02	.59
			Average		-.02	-.04	.69

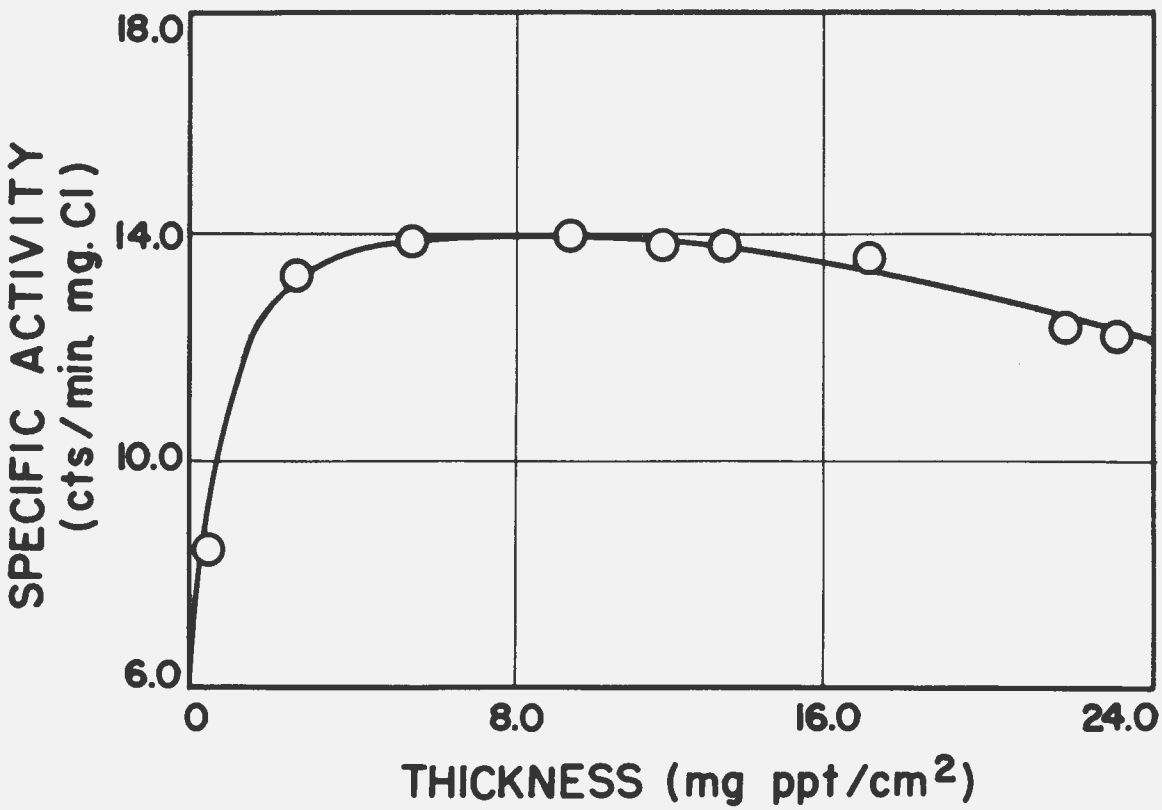

Figure 1. Determination of sample thickness with minimum self-absorption.

Mounting and Counting After weighing, the samples were placed on cardboard (approximately 2 inches square) and covered with cellophane discs (density 2.5 mg per cm.) of the same diameter as the filter discs. The cellophane was attached to the cardboard by means of Scotch tape. Every effort was made to keep the tape on the very edge of the cellophane so that a uniform thickness of material would be above the sample to absorb and scatter the radiation. After securing the sample to the cardboard, it was placed on an aluminum mount in preparation for counting.

All samples were counted for a sufficient length of time so that the standard deviation was less than five per cent of the total counts. A 300 microsecond tube deadtime correction was added to the observed counting rate. The background counting rate was subtracted from this corrected value to obtain the actual counting rate of the sample.

The specific activity, S, was defined as the actual counting rate (corrected to the same sample thickness) divided by the weight of chloride present in the sample. The fraction of exchange, F, is the ratio of specific activities at time "t" and infinite time, S_t/S_∞. The term, half-time of exchange, refers to the time the exchange must be allowed to proceed before "F" becomes equal to one-half.

EXPERIMENTAL DATA

In any exchange reaction it is important to know the concentration of various species that may be present in solution. Water is known to replace the chlorine ligands in tetrachloroplatinate(II) to form an appreciable amount of trichloroaquoplatinate(II).

$$[PtCl_4]^{=} + H_2O \rightleftharpoons [PtCl_3(H_2O)]^{-} + Cl^{-}$$

This aquo-complex functions as a weak acid according to the following equation:

$$[PtCl_3(H_2O)]^{-} \rightleftharpoons [PtCl_3OH]^{=} + H^{+}$$

The rate and extent of this aquation can, therefore, be determined by a pH titration. Several of these titrations were made; a typical example is given in Figure II. A single break in the titration curve was observed. The end-point corresponded to an acid concentration of about 60% of the molar concentration of platinum present in solution. This indicated that in an aged solution containing little or no chloride originally, the major platinum species present in solution was the aquo-complex.

Since the rate of aquation was not available, it was necessary to determine if a significant amount of aquation was occurring during the course

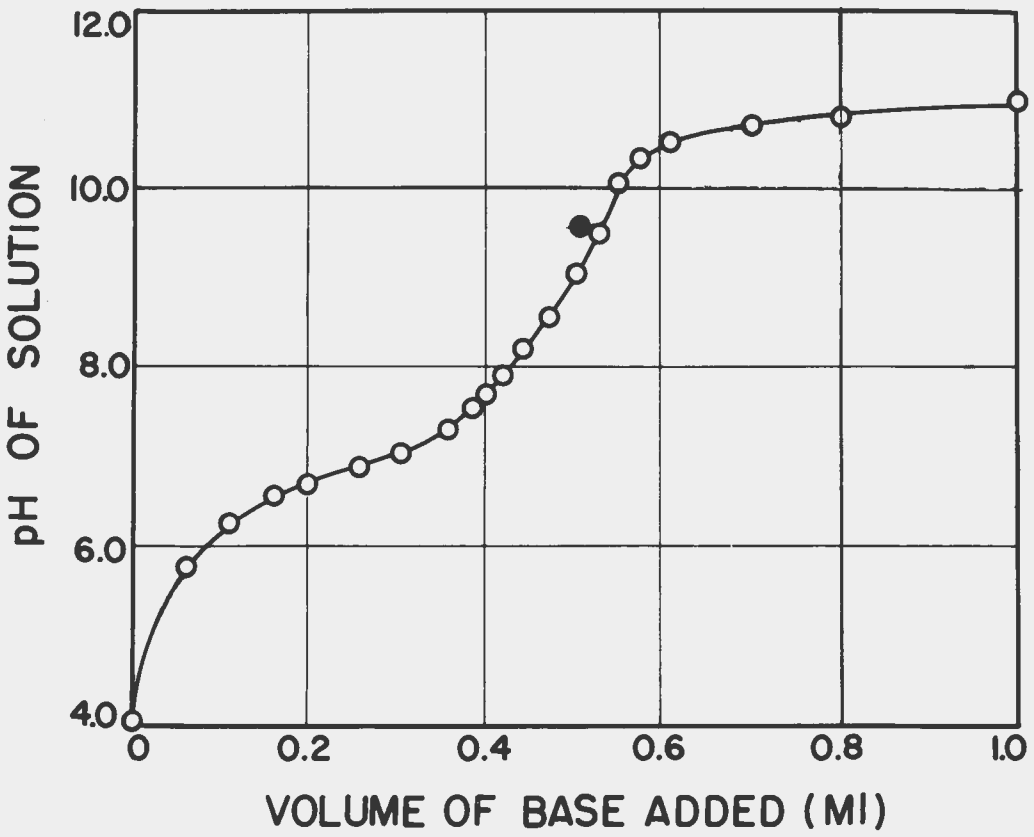

Figure II. pH titration of acid formed in the dissociation of trichloroaquoplatinate(II).

of the pH titration. This was accomplished by using only a portion of the solution that had been allowed to age in the original titration (pH of end-point 9.26). The volume of base required to reach the indicated end-poing of the titration curve (0.503ml) was added to another sample and the pH of the solution was recorded (9.75). This pH reading was considerably higher than the value of the inflection of the titration curve. This would indicate that a significant amount of the acid was formed during the course of the pH titration. The equivalent volume of base needed to neutralize the acid present before the titration began was taken as 0.482 ml. (0.503 x .503/.524 = 0.482).

The following method was used to study the kinetics of this aquation reaction. It was impractical to make several complete titrations to determine the extent of aquation of a sample of $[PtCl_4]^=$ as a function of time. Instead, only enough base was added for each determination to neutralize approximately 40-60% of the acid present. The pH of the solution was recorded immediately. The actual per cent neutralization was obtained from a chart in which pH had been plotted against per cent neutralization determined from a complete, corrected, final titration. This experimental data is given in Table III. The half-time of aquation obtained directly from Figure III was 2.37±0.05 hours. The calculations required to obtain a value for the equilibrium constant and the derivation of f(x) in Figure III and Table III will be discussed in a later section on chemical kinetics.

Magnus' Salt An effective method of removing $[PtCl_4]^=$ from solution was to precipitate it as the Magnus' Salt, $Pt(NH_3)_4PtCl_4$. Magnus first reported this compound in 1828; since then its properties have been characterized. It is a very stable, green, non-hygroscopic, insoluble salt that forms very finely divided crystals when precipitated from aqueous solution. An interesting feature is the unstable pink compound (46,47,48), apparently an isomer of the green substance, that can be prepared. However, this pink form is unstable in contact with aqueous solution. Several workers have attempted to characterize this isomer and to establish the conditions under which it is formed. The pink form (mixed with green) is frequently formed when dry K_2PtCl_4 and $Pt(NH_3)_4(NO_3)_2$ are mixed together and water added. Immediate centrifuging will separate the pink salt from solution before it is converted to the stable green isomer.

Chemical analysis of the Magnus' salt (both pink and green forms) precipitated from a freshly prepared $[PtCl_4]^=$ solution are given in Table IV. Platinum was plated onto a platinum cathode from a 2% sulfuric acid solution. A standard Mohr titration was used to determine the amount of chloride present. A modified Kjeldahl procedure was used to analyze for ammonia. The results indicated that a pure precipitate of $Pt(NH_3)_4PtCl_4$ was obtained from a solution of freshly prepared tetrachloroplatinate(II).

Table III. pH titrations to determine extent of aquation

Age of Solution (hr)	Volume of Base (0.1102N) (ml)	Observed pH	Per Cent Neutralization (%)	Vol. of base Required for complete Neut. (ml)	Concentration $[PtCl_3(H_2O)]^-$ (moles/liter)	f(x)*
0.06	0.020	9.92	109.7	0.018	0.00040	0.949
0.30	0.020	7.38	70.0	0.029	0.00064	0.919
0.72	0.040	7.14	56.7	0.071	0.00156	0.809
1.04	0.050	6.94	47.0	0.106	0.00234	0.721
2.38	0.070	6.71	36.0	0.194	0.00428	0.519
2.88	0.090	6.75	38.3	0.235	0.00518	0.434
3.63	0.090	6.74	37.7	0.239	0.00527	0.425
4.58	0.110	6.65	33.3	0.330	0.00727	0.251
5.08	0.120	6.67	34.0	0.352	0.00776	0.211
5.58	0.120	6.66	33.7	0.356	0.00785	0.203
6.08	0.120	6.62	32.7	0.375	0.00827	0.170
6.58	0.120	6.59	30.8	0.390	0.00860	0.144
7.08	0.120	6.57	30.0	0.400	0.00882	0.128

$$* \; f(x) = \frac{(x_{oo} - x)\left(-x_{oo} + \sqrt{(b + K)^2 + 4Ka}\right)}{x_{oo}\left(x - x_{oo} + \sqrt{(b + K)^2 + 4Ka}\right)}$$

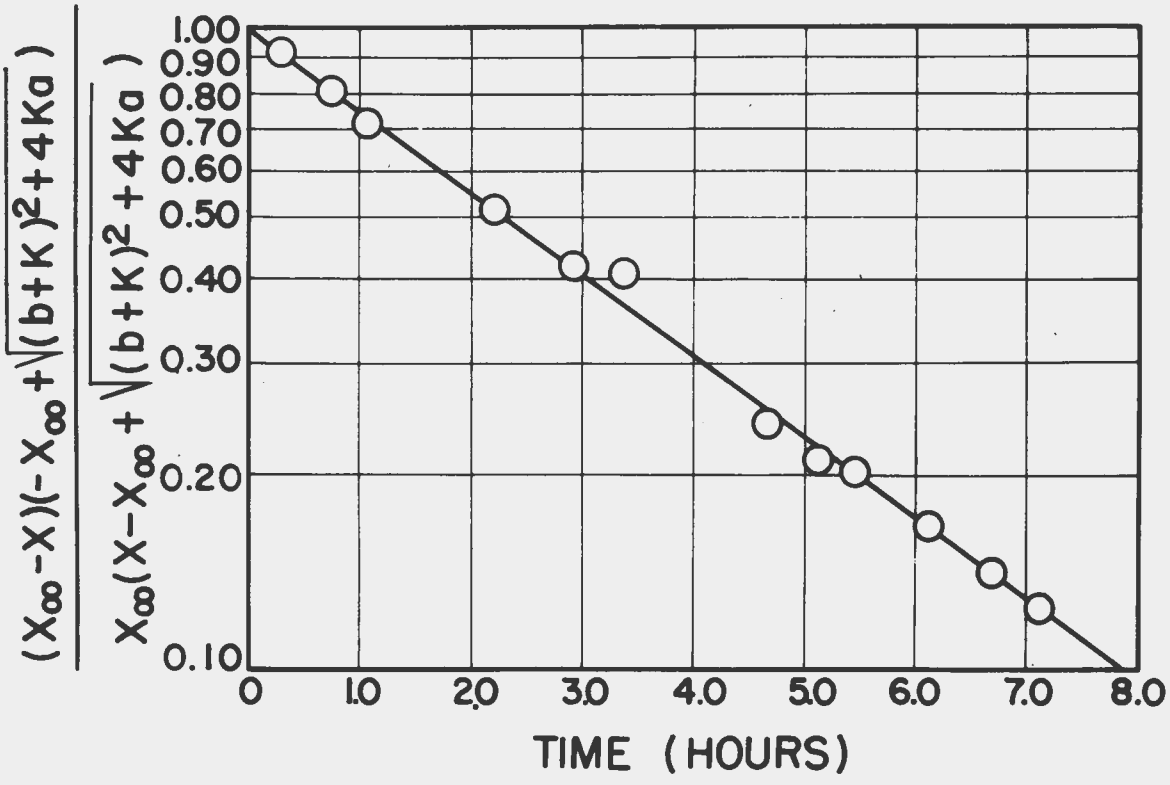

Figure III. The determination of the half-time of aquation of tetrachloroplatinate(II).

Table IV. Analysis of Magnus' Salt preparation

Substance	Magnus' Salt* Analysis Weight Sample (mg)	Per cent Observed	$Pt(NH_3)_4PtCl_4$	$Pt(NH_3)_4PtCl_3(H_2O)_2$	$Pt(NH_3)_4PtCl_3OH$
platinum	203.3	65.27	65.04	64.89	67.09
chlorine	227.6	23.73	23.63	23.57	18.28
ammonia	39.58	11.60	11.34	7.56	11.71
other			0.00	3.98	2.92

*Obtained from freshly prepared K_2PtCl_4 solution

The composition of the precipitate obtained when $Pt(NH_3)_4(NO_3)_2$ was added to an aged solution of K_2PtCl_4 was investigated. Since $[PtCl_3(H_2O)]^-$ and $[PtCl_3OH]^=$ were present in the solution due to aquation and subsequent ionization, the salts $Pt(NH_3)_4[PtCl_3 \cdot H_2O]_2$ and $Pt(NH_3)_4PtCl_3OH$ may have co-precipitated with Magnus' salt. Further indication of co-precipitation was given by the amount of precipitate obtained from an aged $[PtCl_4]^=$ solution with no added chloride. The weight of this precipitate was about twice as great as the weight of $Pt(NH_3)_4PtCl_4$ which could be formed from the $[PtCl_4]^=$ species present in the equilibrium mixture. Calculated analysis of these three platinum compound is given in Table IV. It is to be noted from this table that the ammonia analysis is critical in distinguishing between $Pt(NH_3)_4PtCl_4$ and $Pt(NH_3)_4[PtCl_3 \cdot H_2O]_2$. The platinum and chlorine content of these two compounds is so nearly identical that they are experimentally indistinguishable.

The appearance of precipitates from a fresh and aged solution was different. X-ray powder diagrams indicated the presence of another crystal in the precipitate from an aged solution and the infra red spectrum of the salts indicated the presence of the O-H bond only in the precipitates from an aged solution.

Since the $[PtCl_3OH]^=$ is formed by the hydrolysis of $[PtCl_3(H_2O)]^-$, the pH of the solution should be a convenient means of determining a shift in the relative concentrations of the two substances. The pH of the solution was the same before and after the addition of the precipitating agent. Thus the two species $[PtCl_3(H_2O)]^-$ and $[PtCl_3OH]^=$ occur in the precipitate in approximately the same ratio as they occurred in solution. The pH of an equilibrium solution containing all three chloroplatinate(II) compounds (original concentration of $[PtCl_4]^=$ was .0166 and original chloride concentration was 0) was approximately 4. Therefore the concentration of the $[PtCl_3OH]^=$ was negligible with respect to the other species.

The precipitates obtained, containing various amounts of $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$ species, were analysed for ammonia content. These results are listed in Table V. The calculated ammonia content was based upon the relative amounts of the two species present in solution at equilibrium. The value of the equilibrium constant used in these calculations was 0.0187. A modified Kjeldahl procedure was used to determine the ammonia content of the various precipitates. The calculated and observed percentage compositions given in Table V indicate that, in general, the assumptions made in the calculations were valid.

Actually the fact that a mixture of the two compounds occur in the precipitate did not interfer with the calculations of exchange. The chlorine content of the two salts was the same; hence the specific activities of the samples could be calculated.

Table V. Kjeldahl ammonia analysis of samples containing various amounts of $Pt(NH_3)_4PtCl_4$ and $Pt(NH_3)_4(PtCl_3 \cdot H_2O)_2$ from equilibrium solutions.

Original Concentration K_2PtCl_4 (moles/liter)	Original Concentration KCl (moles/liter)	Final Concentration $[PtCl_3(H_2O)]^-$ (moles/liter)	Absolved Per Cent ammonia	Calculated* Per Cent ammonia	Error Per Cent
0.0083	0.1340	0.0000**	11.60	11.34	+0.26
0.0166	0.0100	0.0081	10.25	9.49	-0.76
0.0166	0.0100	0.0081	9.23	9.49	-0.26
0.0166	0.0100	0.0081	9.59	9.49	+0.10
0.0083	0.0100	0.0043	9.88	9.40	+0.48
0.0083	0.1340	0.0010	10.79	10.55	+0.24

*Assuming equilibrium constant is 0.0187 and platinum species precipitate in the same ratio as they occur in solution.

**Precipitate from a freshly prepared solution.

Table VI. Typical exchange data and calculation for freshly prepared K_2PtCl_4 solutions.

Time allowed for exchange to proceed (hr)	Weight precipitate (mg)	Weight chloride (calc.) (mg.)	Count rate (cts.min)	Corrected count rate (cts/min)	Specific activity (cts/min mg Cl)	Fraction exchange (F)	1-F
0.05	44.0	10.4	104.5	106	10.2	0.031	0.969
0.30	52.2	12.3	185.5	185	15.0	0.046	0.954
2.00	54.4	12.8	400.5	398	31.1	0.091	0.909
4.00	53.3	12.6	695.0	691	54.8	0.171	0.829
5.75	55.1	13.0	1091	1081	83.2	0.260	0.740
12.30	52.9	12.5	1742	1732	138.6	0.433	0.567
19.30	54.5	12.9	2433	2414	187	0.584	0.416
250.00	44.5	10.5	3588	3620	315		
250.00	44.3	10.5	3531	3563	313		

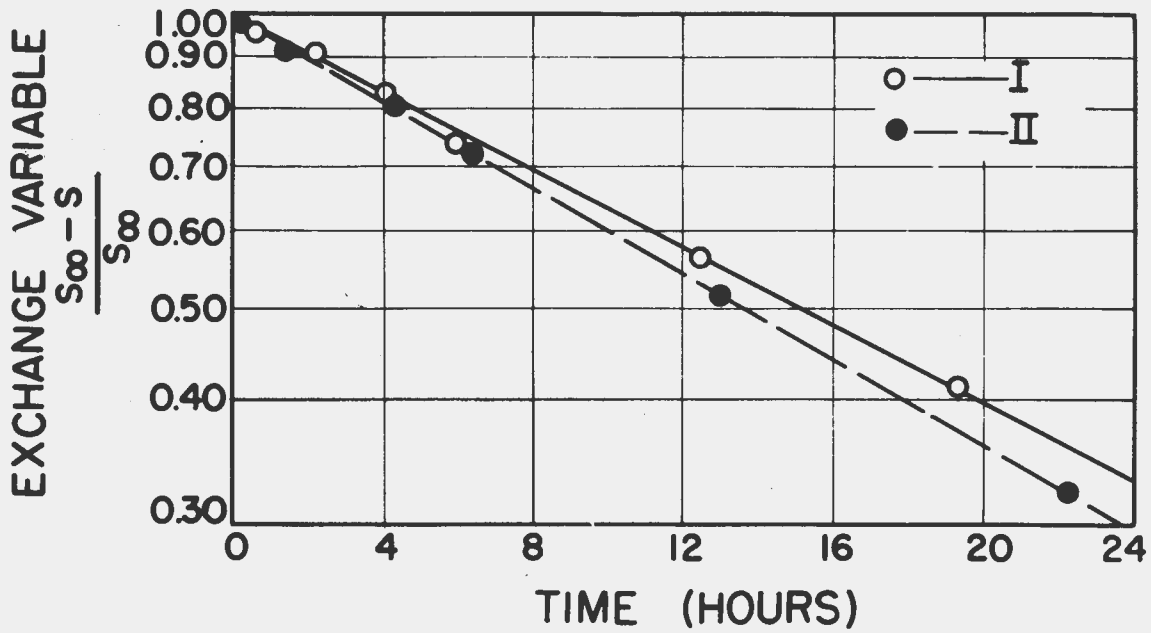

Figure IV. Typical curves used to determine the half-time of exchange of fresh tetrachloroplatinate(II) solutions.

Table VII. Comparison of exchange half-times using freshly prepared K_2PtCl_4 solutions.

	Initial Concentration K_2PtCl_4 (moles/liter)	Initial Concentration KCl^- (moles/liter)	Ionic* Strength	Observed $t_{\frac{1}{2}}$ (hr)	Calculated $t_{\frac{1}{2}}$ (hr)
I	0.00830	0.1340	0.184	15.2	16.9
II	0.00415	0.0638	0.318	13.8	15.0
III	0.01660	0.2680	0.318	15.3	16.8
IV	0.01660	0.0938	0.318	13.2	13.1

*$LiClO_4$ added as inert electrolyte

Fresh Solution The reactants were prepared as described previously in preparation for exchange work using freshly prepared tetrachloroplatinate (II) solutions. The samples were obtained by the regular procedure. Table VI lists the calculations necessary to prepare one of the half-time curves in Figure IV. Notice that in Figure IV the curve passes through 98% at zero time. This indicates that any separation-induced exchange or co-precipitation of chloride was satisfactorily small. Table VII gives the resulting half-time for several experiments completed under various conditions. As indicated in Table VII, the observed half-times were almost independent of concentration of the reactants, therefore the exchange did not proceed via a second order mechanism.

Aged Solution Since the potassium tetrachloroplatinate(II) aquates, it is necessary to determine this effect upon the rate of exchange. Counting samples were obtained from previously described aged tetrachloroplatinate (II) solutions. Figure V gives four of the exchange curves obtained under these conditions. The concentration variables as well as the observed and calculated half-times of exchange are given in Table VIII. Notice that the curves in Figure V passed very nearly through one at zero time; again separation-induced exchange or co-precipitation of chloride was small.

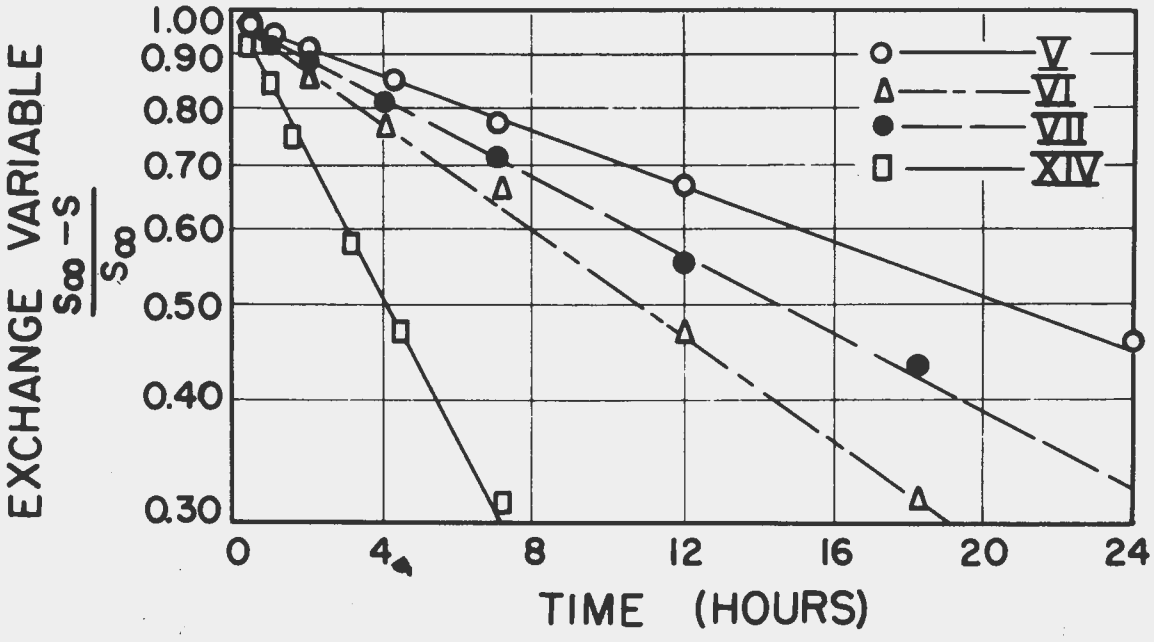

Figure V. Typical curves used to determine the half-time of exchange for aged solution of tetrachloroplatinate(II).

Table VIII. Comparison of exchange half-times using an aged, equilibrium solution of $[PtCl_4]^=$

Exchange number	Time allowed for solution to reach equilibrium (hours)	Concentration of $[PtCl_4]^=$ before ageing "a" (moles/liter)	Concentration of KCl before ageing "b" (moles/liter)	Calculated* concentration of $[PtCl_3(H_2O)]^-$ "x" (moles/liter)	Observed $t_{\frac{1}{2}}$ (hours)	Calculated $t_{\frac{1}{2}}$ (hours)
V	48	0.0166	1.0001	0.0003	15.0	19.2
VI	25	0.0166	0.2684	0.0010	19.0	17.1
VII	48	0.0083	0.1340	0.0010	14.2	17.4
VIII	25	0.0166	0.0938	0.0025	11.7	13.7
IX	23	0.0166	0.0750	0.0031	9.3	12.9
X	23	0.0166	0.0500	0.0042	7.5	11.7
XI	23	0.0166	0.0250	0.0061	5.1	10.1
XII	68	0.0166	0.0100	0.0081	4.3	8.9
XIII	60	0.00415	0.0100	0.0025	5.6	18.1

*Calculated using 0.0187 for equilibrium constant.
Ionic strength 0.318; equilibrium established at 25.0 C.

KINETICS CALCULATIONS

Equilibrium Constant From the data obtained in the pH titration it was possible to calculate the equilibrium constant for the aquation equation.

$$[PtCl_4]^{=} + H_2O \rightleftharpoons [PtCl_3(H_2O)]^{-} + Cl^{-}$$

For simplicity the following terms will be used:

a = original concentration of $[PtCl_4]^{=}$ (moles/liter)
b = original concentration of Cl^{-} (moles/liter)
x = concentration of $[PtCl_3(H_2O)]^{-}$ (moles/liter)
(a - x) = concentration of $[PtCl_4]^{=}$ (moles/liter)
(b + x) = concentration of Cl^{-} (moles/liter)
K = equilibrium constant (moles/liter)

The equilibrium constant was given by the expression

$$K = x_\infty (b + x_\infty)/(a - x_\infty) \tag{1}$$

and was calculated (see the data in Table III) to have a value of 0.0187. This equation can be rearranged to give an explicit expression for x_∞.

$$x_\infty = \frac{-(b + K) + \sqrt{(b + K)^2 + 4Ka}}{2} \tag{2}$$

Chemical Equilibrium Since aquation occurred in solutions containing $[PtCl_4]^{=}$, Cl^{-} and possibly inert electrolytes and since it was necessary to know the concentration of the particular species at any given time, an expression was derived which predicted the concentration of $[PtCl_3(H_2O)]^{-}$, x, as a function of time, t.

Let R_1 and R_2 be the rate (moles/liters hours) of the forward and the reverse reactions, respectively, in the above equation. These rates were assumed to be given by the expression.

$$R_1 = k_1(a + x) \tag{3}$$

$$R_2 = k_2(x)\ (b + x) \tag{4}$$

Where k_1 and k_2 are specific reaction velocity constants. The equilibrium constant, K, would then equal k_1/k_2.

$$dX/dt = R_1 - R_2 = k_1(a - x) - k_2(x)\ (b + x) \tag{5}$$

$$\int_0^x dx/\left[x^2 + (b + K)x + Ka\right] = -\int_0^t k_2\, dt \qquad (6)$$

$$-k_2 t\ \sqrt{(b+K)^2+4Ka} = \ln \frac{(x-x_\infty)\,(x_0-x_\infty+\sqrt{(b+K)^2+4Ka})}{(x_0-x_\infty)\,(x-x_\infty+\sqrt{(b+K)^2+4Ka})} \qquad (7)$$

$$x = x_\infty (1 - e^{-k_2 bt}) \qquad x_\infty \ll a \qquad x_0 = 0 \qquad (8)$$

Equation (7) was used for experimental evaluation of the rate constants at 25°C (See Table III, Figure III). In this experiment for which $x_0 = 0$, the indicated logarithmic function gave a satisfactory straight line corresponding to a half-time of 2.37±05 hours. Using this result, k_2 was calculated to be 7.35 liters/mole-hour and k_1 (equal to k_2K) was 0.137 $hour^{-1}$.

Exchange Kinetics The fact that $[PtCl_4]^=$ undergoes a reversible aquation to form $[PtCl_3(H_2O)]^-$ presents one mechanism of exchange, for the reverse reaction will introduce radioactive atoms into the complex. The kinetics for this single mechanism of exchange follows. For this treatment it is necessary to consider the number of radioactive chlorine atoms, Cl^*, present in the form of Cl^-; $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$. These additional terms must be defined.

u = atoms of Cl^* in $[PtCl_4]^=$ per ml of solution
v = atoms of Cl^* in $[PtCl_3(H_2O)]^-$ per ml of solution
w = atoms of Cl^* in Cl^- per ml of solution
$I = u + v + w$
$S_u = u/4(a - x)$; Specific activity of $[PtCl_4]^=$
$S_v = v/3(x)$; Specific activity of $[PtCl_3(H_2O)]^-$
$S_w = (I - u - v)/(b + x)$; Specific activity of Cl^-

If the only exchange occurs by means of the reversible aquation of $[PtCl_4]^=$, then the following general equations apply:

$$du/dt = -4R_1 S_u + R_2(3S_v + S_w) \qquad (9)$$

$$dv/dt = 3R_1 S_u - 3R_2 S_v \qquad (10)$$

Using the rate of expression of equations (3) and (4) these equations become:

$$du/dt = -k_1 u + k_2 bv + k_2 x(I-u-v) \qquad (11)$$

$$dv/dt = 3(k_1 u)/4 - k_2 bv \qquad (12)$$

In the special case of a freshly prepared solution x is necessarily small ($x_0 = 0$), v is approximately zero and it is assumed that dv/dt is negligibly small.

$$du/dt = -(k_2x + k_1/4) + k_2xI \quad (13)$$

$$du/dt = -k_2(x+K/4) + k_2xI \quad (14)$$

To approach isotopic equilibrium, the aquation reaction and its reverse reaction must occur at least four times for each platinum complex, one for each of the four chlorines. A major portion of the exchange occurs in a system very close to chemical equilibrium, i.e., most of the exchange will take place after $x \approx x_\infty$.

$$u = u_\infty [1 - e^{-k_2(x_\infty + K/4)t}] \quad (15)$$

$$t_{\frac{1}{2}} = .693/[k_2(x_\infty + K/4)] \quad (16)$$

Comparison of the calculated values to the observed values for the half-time of exchange in Table VII indicates that this mechanism is adequate in explaining the exchange for these conditions. The general trend of the half-times is given correctly and the difference of approximately 5% between the experimental and calculated half-times are consistent with the experimental accuracy.

Aged Solutions Several determinations of the half-times of exchange were made using aged solutions of tetrachloroplatinate(II). The two platinum species, $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$, were allowed to approach equilibrium by standing for several hours before exchange measurements were begun. In this way a steady state, with regard to the aquation reaction, was established before the radioactive chloride was added. Since the volume of solution and the amount of tracer chloride added were negligible in comparison to the total volume and the total amount of chloride present in solution (less than 2% of the total chloride), the $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$ could be assumed to exist in equilibrium throughout the course of the exchange. The kinetics of this "steady state" system is described below.

Since equations (9) and (10) are general, they also apply to these aged systems. They can be rearranged to the following:

$$(du/dt)(1/R) = -[u/(a-x)] + [v/x] + [(I-u-v)/(b+x)] \quad (17)$$

$$(dv/dt)(1/R) = [(3u)/(4a-4x)] - [v/x] \quad (18)$$

The solution of these equations is of this form:

$$u = u_\infty + A_1e^{\alpha_1 t} + A_2e^{\alpha_2 t} \quad (19)$$

$$v = v_\infty + B_1e^{\alpha_1 t} + B_2e^{\alpha_2 t} \quad (20)$$

Table IX. Calculated values of constant incurred in integration

Exchange number	a - x	x	A_1	A_2	B_1	B_2	α_1	α_2	R'/R
V	0.0163	0.0003	-0.0612	-0.0000	-0.0008	0.0000	-0.0360	-8.0061	
VI	0.0156	0.0010	-0.1862	-0.0002	-0.0092	0.0002	-0.0407	-2.2331	
VII	0.0074	0.0010	-0.1755	-0.0007	-0.0190	0.0006	-0.0385	-1.0988	
VIII	0.0141	0.0025	-0.3481	-0.0030	-0.0505	0.0029	-0.0501	-0.8685	
IX	0.0135	0.0031	-0.3756	-0.0057	-0.0716	0.0054	-0.0537	-0.7125	
X	0.0124	0.0042	-0.4131	-0.0144	-0.1206	0.0134	- .0590	-0.5295	0.56
XI	0.0105	0.0061	-0.4055	-0.0537	-0.2481	0.0477	- .0687	-0.3575	0.95
XII	0.0085	0.0081	-0.2728	-0.1607	-0.4618	0.1328	-0.0743	-0.2599	1.0
XIII	0.0017	0.0025	-0.2009	-0.0489	-0.3231	0.0426	-0.0375	-0.2198	2.8

The constants (A_1, A_2, B_1, B_2, α_1, and α_2) incurred in the solution of these equations can be evaluated. These calculated values, together with the experimental conditions, are given in Table IX.

Since the measured activity occurs in both $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$, equations (19) and (20) could be combined.

$$u+v = u_\infty + v_\infty + (A_1+B_1)e^{\alpha_1 t} + (A_2+B_2)e^{\alpha_2 t} \qquad (21)$$

From Table IX it can be seen that the coefficient for the short component (A_2+B_2) is negligible. Therefore, only one period in the exchange half-time curves (given in Figure V) should be present. Since the Curves (V) & (VI) obtained under these conditions, appear as a single exponential, Equation (21) could, therefore, be rewritten:

$$u+v = u_\infty + v_\infty + (A_1+B_1)e^{\alpha_1 t} \qquad (22)$$

Under these conditions equation (22) could be simplified to give the usual logarithmic exchange curve.

$$\ln[(u_\infty - u)/u_\infty] = -\alpha_1 t \qquad (23)$$

The calculated half-times listed in Table VIII agreed with observed half-times of exchange as long as the original chloride concentration of the solution was high enough to suppress the aquation reaction ($a \gg x$). Under this condition the exchange could be explained by the simple aquation mechanism. There was, therefore, no evidence of a possible second order exchange between Cl^{*-} and $[PtCl_4]^=$.

In solutions of low original chloride concentration ($b < 0.1$) the observed exchange half-times were shorter than the calculated half-times. Whenever there was a significant amount of $[PtCl_3(H_2O)]^-$ in solution, the exchange half-time was decreased significantly from the value which was predicted by equation (21). It appeared that under these conditions the exchange mechanism was more complex and that $[PtCl_3(H_2O)]^-$ exchanged chlorine with the radioactive chloride in solution. This reaction could be written as:

$$[PtCl_3(H_2O)]^- + Cl^{*-} \xrightarrow{R'} [PtCl_2Cl^*(H_2O)]^- + Cl^-$$

Where R' is the rate of reaction (mole/liter-hour) and is a constant under steady state conditions.

The rate equation for u, (15), remained the same; however, an additional term was required for v to account for this additional exchange with $[PtCl_3(H_2O)]^-$. The rate equation for v could be written:

$$dv/dt = R[3u/(4a-4x)]-R[v/x]+R'[(I-u-v)/(b+x)]-R'[v/3x] \quad (24)$$

Again the solution of Equations (17) and (24) was of the form:

$$u = u_\infty + A_1' e^{\alpha_1' t} + A_2' e^{\alpha_2' t} \quad (25)$$

$$v = v_\infty + B_1' e^{\alpha_1' t} + B_2' e^{\alpha_2' t} \quad (26)$$

The value for α_1', and α_2' and the coefficients ($A_1' + B_1'$ and $A_2' + B_2'$) were calculated for a number of values of R'/R. In regions of moderate values of the ratio R'/R, the solution in some cases, gave significant values for the coefficients of both exponential terms. Over the regions in which "F" could be followed accurately, the calculated semi-log plots appeared nearly straight with a half-time less than the half-time of the long period component. Values of R'/R for the various experiments were evaluated by a trial and error method to find the values which gave the observed half-times of the exchange reactions. Thus a relative estimate of the importance of the two exchange mechanisms could be ascertained. These values of R'/R are given in Table IX.

The results indicate that in aged solutions containing only a very small amount of chloride originally ($b \leq 0.01$ molar), the direct exchange of chloride with $[PtCl_3(H_2O)]^-$ is a very significant mechanism.

This direct exchange with $[PtCl_3(H_2O)]^-$ appeared to be first order in $[PtCl_3(H_2O)]^-$. Values of R'/R for a series of experiments are shown in Fig. 7 including in part the experiments in Tables VIII and IX. If the rate of the additional exchange process has the form

$$R' = k' [PtCl_3(H_2O)^-][Cl^-]^n \quad (27)$$

then R'/R will be given by the expression

$$R'/R = k'/k_2 \, (b+x)^{1-n} \quad (28)$$

It can be seen from Fig. 7 that the points lie along the curve which is a plot of the function, $1/(b+x)$. The value of n is therefore zero and the exchange of $[PtCl_3(H_2O)]^-$ with chloride is first order in the concentration of the complex and independent of chloride. The best value of k' for this first order exchange, taken from all the data, was 0.16 hrs^{-1}. It is approximately equal to k_1, the first order rate constant for the aquation of $[PtCl_4]^=$. A possible path for this additional exchange may be the reversible substitution of a chloride in the trichloroaquoplatinate(II) by a water molecule. This second aquation (32) has been observed; although, it appears rather insignificant.

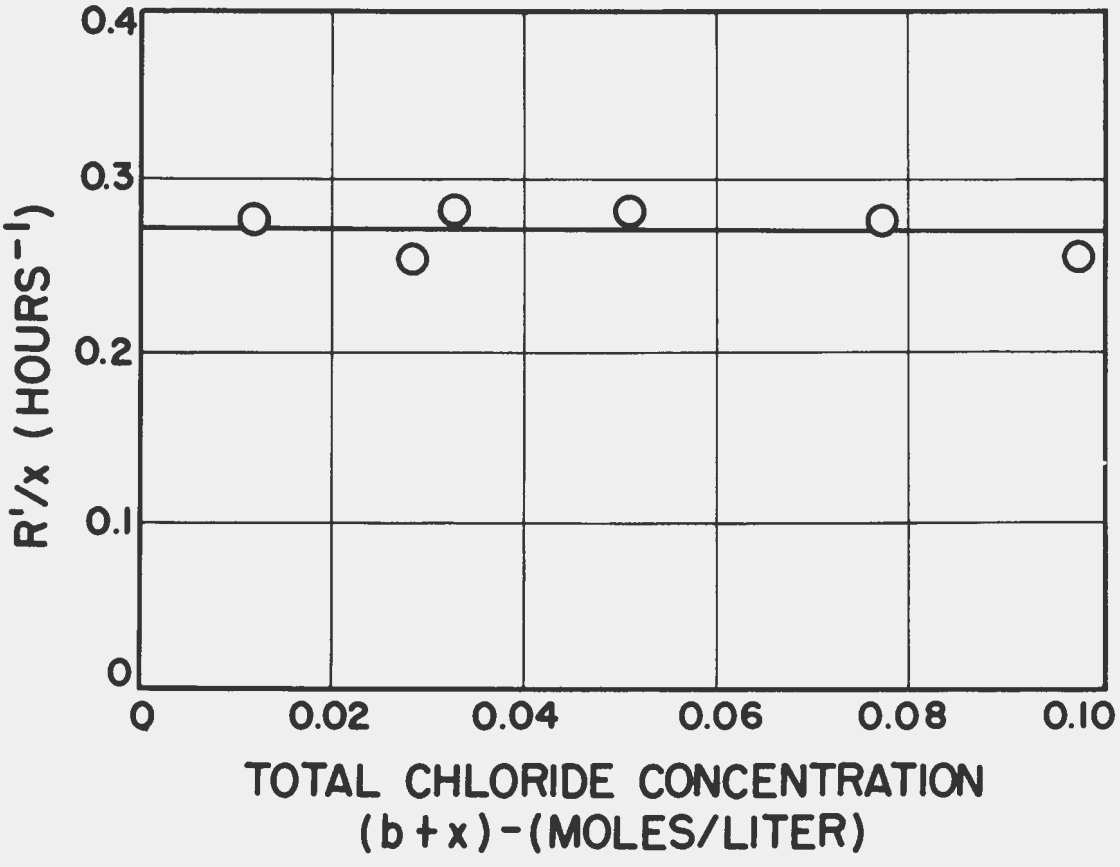

Figure VI. Effect of chloride concentration on the rate of exchange of trichloroaquoplatinate(II).

SUMMARY

Tetrachloroplatinate(II) is unstable towards aquation in an aqueous solution; however, the extent of the aquation can be measured accurately by a pH titration. The precipitate formed when tetraammineplatinum(II) is added to an aged solution of tetrachloroplatinate(II) is a mixture of salts but, nevertheless, the precipitate can be used in determining the amount of activity in the platinum complexes. With this method the extent of exchange between the chlorocomplexes of platinum and tagged chloride has been followed under different conditions. In case of low concentration of trichloraquoplatinate(II) the reversible aquation of tetrachloroplatinate(II) has been found to be the only mechanism giving an appreciable exchange. However, the data have shown that the trichloroaquoplatinate(II) undergoes an exchange of chlorine with chloride with a rate which is first order in the concentration of the trichloroaquoplatinate(II) and probably independent of the chloride concentration.

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